



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>4</sup> :</b> C09K 21/14, C08K 3/34 C08L 29/14, 61/28	<b>A1</b>	<b>(11) International Publication Number:</b> WO 88/ 05804 <b>(43) International Publication Date:</b> 11 August 1988 (11.08.88)
<b>(21) International Application Number:</b> PCT/GB88/00055 <b>(22) International Filing Date:</b> 29 January 1988 (29.01.88) <b>(31) Priority Application Number:</b> 8702011 <b>(32) Priority Date:</b> 29 January 1987 (29.01.87) <b>(33) Priority Country:</b> GB  <b>(71) Applicant:</b> DIXON INTERNATIONAL LIMITED [GB/GB]; Pampisford, Cambridge CB2 4HG (GB). <b>(72) Inventor:</b> MILNER, Bruce, Alan ; 8 Brookfield Road, Sawston, Cambridge (GB). <b>(74) Agent:</b> EDWARD EVANS & CO.; Chancery House, 53-64 Chancery Lane, London WC2A 1SD (GB).		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FIRE-RESISTANT COMPOSITION  <b>(57) Abstract</b>  A plastic composition which at least when hardened is resistant to fire comprises: a binder comprising a flexible film-forming adhesive polymer, such as polyvinylbutyral, in a volatile solvent, preferably a non-flammable volatile solvent such as trichloroethane, the binder having dispersed therein a fire retardant such as aluminium trihydrate, an exfoliatable mineral, such as vermiculite, and preferably also a thixotropic agent such as precipitated silica.		

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Fire-resistant composition

The present invention relates to a composition which at least when hardened is resistant to fire. In particular, but not exclusively, the composition may be a plastic composition which hardens on exposure to air. Such a plastic composition may be used as a sealant or mastic, in particular to seal around pipes, wires or ducts or other services where they pass through walls or partitions.

In accordance with the present invention there is provided a plastic composition which comprises: a binder comprising a flexible film-forming adhesive polymer in a volatile solvent, the binder having dispersed therein a thixotropic agent, a fire retardant and an exfoliatable mineral.

On exposure of the composition to air the volatile solvent evaporates causing the composition to harden.

The adhesive polymer may be polyvinyl butyral.

The volatile solvent is preferably non-flammable.

The volatile solvent may be trichloroethane. Trichloroethane evaporates sufficiently quickly in air at ambient temperature (i.e. 18-24°C), is non-toxic or of low toxicity and is non-flammable.

The thixotropic agent, which may be precipitated silica, serves to prevent slumping of the composition in use. It is envisaged that the thixotropic agent may be omitted in certain circumstances.

The fire retardant may be aluminium trihydrate. Aluminium trihydrate acts as a fire retardant by giving off water vapour leaving aluminium oxide, which is refractory and which, when exposed to high temperature, can combine with other inorganic

material present to form a hard fire retardant crust. Such other inorganic material may include the thixotropic agent and the exfoliatable mineral.

The exfoliatable mineral may be vermiculite, which exfoliates when heated above 250°C giving a heat-insulating material.

The binder preferably comprises dispersed therein a carbonific. The carbonific may be an organic polyhydroxy compound such as pentaerythritol.

The binder preferably contains dispersed therein a formaldehyde resin such as melamine formaldehyde resin.

In addition to the formaldehyde resin the binder preferably contains dispersed therein a cross-linking agent for the resin. The cross-linking agent may be a polyamido compound such as dicyandiamide. At elevated temperature the formaldehyde resin is cross-linked by the cross-linking agent and acts as an additional binder. At even higher temperature the formaldehyde resin decomposes to form a carbonaceous char which enhances the fire-resistance of the composition. Thus the formaldehyde resin serves at least in part as the carbonific.

To accelerate the rate at which the carbonific (e.g. the cross-linked formaldehyde resin and/or polyhydroxy compound) decomposes at high temperature and/or to reduce the temperature at which the cross-linked formaldehyde resin begins to decompose, the binder may contain dispersed therein an activator which promotes the decomposition of the resin.

The activator is preferably an ammonium phosphate such as monoammonium phosphate.

The binder may further contain dispersed therein a water-hardenable

setting agent such as Plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ). The setting agent, by reaction with atmospheric water, aids in the hardening of the composition when exposed to air, acts as a filler and by giving off water vapour when heated assists in making the hardened 5 composition fire resistant.

The binder may further contain dispersed therein a potassium, sodium aluminosilicate to prevent premature curing or hardening as a result of possible dampness in one or more of the ingredients such as the ammonium phosphate and the formaldehyde resin.

- 10 The binder may include castor oil to improve the flexibility and damp resistance of the hardened composition.

Preferred proportions, in parts by weight, of the various ingredients of the composition according to the invention are given below.

15 Ingredient	Preferred proportions	More preferred proportions
Monoammonium phosphate	8 - 20	10 - 18
Dicyandiamide	3 - 12	5 - 10
Melamine formaldehyde		
20 resin (uncured)	7 - 16	9 - 14
Plaster of Paris	2 - 6	3 - 5
Pentaerythritol	1.5 - 4	2 - 3.5
K,Na alumino-		
silicate (e.g. Silosiv A4)	3 - 8	4 - 6
25 Vermiculite (exfoliating)	4 - 12	6 - 10
Aluminium trihydrate	4 - 12	6 - 10
Polyvinyl butyral	3 - 8	4 - 6
Trichloroethane	20 - 40	25 - 35
Castor oil	1.5 - 4	2 - 3

Precipitated

silica (e.g. Aerosil)	0.5 - 2	0.5 - 1.5
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The above parts by weight are based on a total of 100 parts by weight of the specified ingredients.

5 In addition the composition may include one or more inorganic fillers such as transition metal borates (e.g. zinc, copper and iron borates), china clay, zeolites, alumina, and other common mineral fillers containing aluminium and silicon.

The composition may comprise, dispersed in the binder, expandable  
10 graphite as a filler.

The desired consistency of composition depends on the intended use of the composition. The composition may be formulated to have whatever consistency is desired. However, in general the composition is preferably formulated to be of the consistency of a  
15 conventional mastic and to be extrudable from a conventional mastic extrusion gun.

The invention includes within its scope not only the plastic compositions described above but also the hardened composition resulting from exposing the plastic composition to air.

20 The invention is illustrated by the following example.

Example

The following ingredients were mixed together in the proportions (parts by weight) given.

Ingredient	Amount
25 Monoammonium phosphate	14.6
Dicyandiamide	7.0

Melamine formaldehyde resin	13.2
Plaster of Paris	3.8
Pentaerythritol	2.7
Silosiv A4	5.0
5 Vermiculite (low temperature exfoliating)	7.0
Aluminium trihydrate	7.0
Polyvinyl butyral	5.5
Trichloroethane	30.7
10 Castor oil	2.4
Aerosil	1.0

The composition had the consistency of a conventional mastic.

The composition hardened on exposure to air.

The composition of this example can be used (before hardening) to  
15 seal around service items such as pipes, cable trays and ducts where they penetrate or pass through the inner walls of buildings. The material hardens rapidly on exposure to air, with minimal slumping, by evaporation of the trichloroethene, to give an airtight seal around the penetrating item.

20 On subjecting the hardened composition to elevated temperature under fire conditions, it intumesced (expanding to 2 to 3 times its original volume) and formed a fire resistant sinter which could act as a fire barrier, that is a barrier to flames and hot gases. The sinter had a good heat-insulation value.

25 Tests were carried out as described below. Tests 1 to 4 were independent tests carried out by The Loss Prevention Council (LPC), formerly known as FIRTO, in accordance with British Standard 476 Part 8, 1972. In accordance with the time/temperature curve of this British standard, the temperature is 930°C after 1 hour and  
30 1040° after 2 hours.

### Test 1

In this test, the composition of the example was used to seal around a 75 mm diameter steel pipe passing through a 110 mm square hole in a 225 mm thick brick wall. After hardening of the composition it was found that the seal satisfied both the insulation and integrity requirements of the British Standard over a four hour period.

### Test 2

Integrity ratings for mastic filling the cross section of 20 x 200 mm apertures in a 3 m lightweight aerated concrete block wall having a thickness of 100 mm were measured.

The wall formed one wall of a furnace. The internal furnace pressure was 30 Pa (gauge).

The mastic was the composition of the invention and was supplied into the apertures to fill the cross-section of the apertures and seal the apertures and then allowed to harden. The length of the bead of mastic in each aperture is referred to below as the depth of mastic.

Results were as follows:

20	Depth of mastic	Integrity rating
	25 mm	78 minutes
	50 mm	130 minutes

### Test 3

This test was carried out similarly to the Test 2 except that the mastic was used as a sealant around a 76 mm outside diameter steel pipe passing through a 105 mm square hole in the block wall. The mastic filled the entire length of the hole.



The integrity rating was greater than 130 minutes.

#### Test 4

This test was carried out similarly to Test 3 except that the mastic was used as a sealant around a 105 mm PVC pipe fitted with a 5 pipe closer collar in a 150 mm square hole in the block wall.

The pipe closer collar comprised three 2 mm thick layers of flexible graphite-based intumescent material (as described in Example 1 of our International patent application no. PCT/GB87/00650), giving a total thickness of 6 mm of intumescent material, underneath a 115 mm long x 0.06 mm thick steel collar fastened onto the pipe with clips.

The integrity rating was greater than 130 minutes.

#### Test 5

Six 2" x 2" holes in a 4 sq. ft. Monolite test panel were filled with the composition of the example. After hardening the composition was tested in accordance with ASTM 814/81.

In a first part of this testing procedure, the test panel was subjected to a one hour fire test in accordance with a time/temperature curve as specified. Then the test panel containing the composition was subjected to a stream of water from a fire hose, the water discharging at a pressure of 30 psi (210 kPa) from a 1½" diameter nozzle at a distance of 20' from the centre of the test panel. The water was discharged from the nozzle at the panel for 1½ seconds per square foot of exposed area of the hot panel.

25 The refractory plugs formed by the hardened composition were held sufficiently strongly not to be dislodged by the force of the stream of water and no water passed through to the unexposed face of the panel.

In a second part of the testing procedure, a similarly filled panel was subjected to the same heating procedure for two hours. The seals formed by the hardened composition at the unexposed face of the panel remained intact for all six specimens of the hardened composition. Thus the integrity criteria of the standard were satisfied.

It has been found that the plastic composition of the invention, at least as described in the example, is sticky and adhesive but not tenaciously so. Therefore the composition is best used in confined situations.

The composition of the invention, at least as described in the example, is not adversely affected by low temperature.

Also the composition of the invention, at least as described in the example, does not shrink significantly on hardening.

15 It is envisaged that the composition of the invention may be used for glazing panels and ventilators, in addition to sealing around items passing through walls and partitions.

CLAIMS

1. A plastic composition which at least when hardened is resistant to fire, comprising: a binder comprising a flexible film-forming adhesive polymer in a volatile solvent, the binder  
5 having dispersed therein a fire retardant and an exfoliatable mineral.
2. A composition according to claim 1, wherein the binder also has dispersed therein a thioxotropic agent.
3. A composition according to claim 2, wherein the  
10 thioxotropic agent is precipitated silica.
4. A composition according to any preceding claim, wherein the adhesive polymer is polyvinyl butyral.
5. A composition according to any preceding claim, wherein the volatile solvent is non-flammable.
- 15 6. A composition according to any preceding claim, wherein the volatile solvent is trichloroethane.
7. A composition according to any preceding claim, wherein the fire retardant is aluminium trihydrate.
8. A composition according to any preceding claim, wherein the  
20 exfoliatable mineral is vermiculite.
9. A composition according to any preceding claim, wherein the binder comprises, dispersed therein a carbonific.
- 4 10. A composition according to any preceding claim, wherein the binder contains dispersed therein a formaldehyde resin.

11. A composition according to any preceding claim, wherein the binder contains dispersed therein a cross-linking agent for the resin.
12. A composition according to any preceding claim, wherein the binder contains dispersed therein an activator which promotes the decomposition of the resin.
13. A composition according to any preceding claim, wherein the binder contains dispersed therein a water-hardenable setting agent.
14. A composition according to any preceding claim, wherein the binder contains dispersed therein a potassium, sodium aluminosilicate.
15. A composition according to any preceding claim, wherein the binder includes castor oil.
16. A composition according to any preceding claim, including at least one inorganic filler.
17. A composition according to any preceding claim, comprising dispersed in the binder expandable graphite as a filler.
18. A composition according to any preceding claim, formulated to be of the consistency of a conventional mastic and to be extrudable from a conventional mastic extrusion gun.
19. A composition according to any preceding claim, comprising the following ingredients in the stated proportions by weight based on a total of 100 parts by weight of said ingredients:

Ingredient	Proportions
25 Monoammonium phosphate	8 - 20

Dicyandiamide	3 - 12
Melamine formaldehyde resin (uncured)	7 - 16
Plaster of Paris	2 - 6
5 Pentaerythritol	1.5 - 4
K,Na alumino-silicate	3 - 8
Vermiculite (exfoliating)	4 - 12
Aluminium trihydrate	4 - 12
Polyvinyl butyral	3 - 8
10 Trichloroethane	20 - 40
Castor oil	1.5 - 4
Precipitated silica	0.5 - 2

20. A composition according to any preceding claim, when hardened by exposure to air.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 88/00055

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> : C 09 K 21/14; C 08 K 3/34; C 08 L 29/14; C 08 L 61/28														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC<sup>4</sup></td> <td style="padding: 5px;">C 08 K; C 08 L; C 09 D; C 09 K</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	IPC <sup>4</sup>	C 08 K; C 08 L; C 09 D; C 09 K								
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IPC <sup>4</sup>	C 08 K; C 08 L; C 09 D; C 09 K													
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category <sup>9</sup></th> <th style="width: 60%; padding: 5px;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 30%; padding: 5px;">Relevant to Claim No. <sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">GB, A, 2095683 (DIXON INTERNATIONAL) 6 October 1982 see claims; example 1A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-20</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0139401 (DIXON INTERNATIONAL) 2 May 1985</td> <td></td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 10px;">-----</td> </tr> </tbody> </table>			Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	GB, A, 2095683 (DIXON INTERNATIONAL) 6 October 1982 see claims; example 1A	1-20	A	EP, A, 0139401 (DIXON INTERNATIONAL) 2 May 1985		-----		
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center; padding: 5px;">20th April 1988</td> <td style="text-align: center; padding: 5px;">19 MAY 1988</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center; padding: 5px;">   <b>P.C.G. VAN DER PUTTEN</b> </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	20th April 1988	19 MAY 1988	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	 <b>P.C.G. VAN DER PUTTEN</b>				
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8800055

SA 20458

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/05/88  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2095683	06-10-82	US-A- 4645782	24-02-87
EP-A- 0139401	02-05-85	GB-A, B 2147597	15-05-85
		US-A- 4636538	13-01-87
		CA-A- 1224579	21-07-87